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Review

Heterogeneous Electro-Fenton as “Green” Technology for Pharmaceutical Removal: A Review

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Abstract: The presence of pharmaceutical products in the water cycle may cause harmful effects such as morphological, metabolic and sex alterations in aquatic organisms and the selection/development of organisms resistant to antimicrobial agents. The compounds’ stability and persistent character hinder their elimination by conventional physico-chemical and biological treatments and thus, the development of new water purification technologies has drawn great attention from academic and industrial researchers. Recently, the electro-Fenton process has been demonstrated to be a viable alternative for the removal of these hazardous, recalcitrant compounds. This process occurs under the action of a suitable catalyst, with the majority of current scientific research focused on heterogeneous systems. A significant area of research centres working on the development of an appropriate catalyst able to overcome the operating limitations associated with the homogeneous process is concerned with the short service life and difficulty in the separation/recovery of the catalyst from polluted water. This review highlights a present trend in the use of different materials as electro-Fenton catalysts for pharmaceutical compound removal from aquatic environments. The main challenges facing these technologies revolve around the enhancement of performance, stability for long-term use, life-cycle analysis considerations and cost-effectiveness. Although treatment efficiency has improved significantly, ongoing research efforts need to deliver economic viability at a larger scale due to the high operating costs, primarily related to energy consumption.

Keywords: electro-Fenton; heterogeneous catalyst; pharmaceuticals; aqueous solution



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1. Introduction

Anthropogenic activities are considered a significant threat to the ecological environment with unsustainable development practices leading to deterioration in the surface water resource quality and as such, contamination issues for drinking water supply [1]. Therefore, growing awareness of environmental concerns has prompted the introduction of new legislation in order to preserve the environment and natural resources. The 2030 Agenda for Sustainable Development Goals, approved by all United Nations Member States in 2015, includes a specific aim focusing on the provision of safe and clean drinking water—with the protection of water sources a critical component [2].

More than 700 emerging pollutants and their derivatives have been detected in the European aquatic environment [3]. These included heavy metals and biological contaminants, as well as synthetic organic pollutants and emerging pollutants such as pharmaceuticals (both prescription and over-the-counter drugs), personal care products, flame retardants, cationic surfactants, life-style products (caffeine and nicotine), industrial additives and agrochemicals.

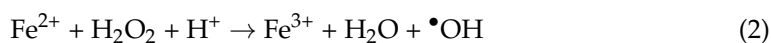
The range of pharmaceutical products may be classified into antibiotics, nonsteroidal anti-inflammatory drugs (NSAIDs), β -blockers, contrast agents, anticonvulsants, hormones

and lipid regulators [4], with antibiotics and NSAIDs most commonly reported as water pollutants due to their high use for clinical purposes (Table 1) [5]. The increasing demand for new drugs has resulted in more than 3000 pharmaceuticals being produced, with new chemical and biologically active molecules being released into the environment. Pharmaceutical products have been detected in many aqueous resources such as surface water, wastewater and even drinking water at concentrations ranging up to 10 µg/L [4]. The primary route of entry to the environment is from effluents generated on pharmaceuticals industries, hospitals and houses (containing both parent compound and metabolites excreted by animals and humans) with a minor contribution from the inappropriate disposal of expired drugs [6]. In addition, urban runoff and leaching from agricultural land contribute to the flow of drugs into the groundwater streams [7]. Given the potential harmful effects of these emerging pollutants, European Directives 2015/495/EU and 2018/840/EU include antibiotics such as amoxicillin and ciprofloxacin requiring testing to monitor their occurrence, distribution, frequency and inclusion in risk assessment.

The main methods widely used for the removal of pharmaceutical products in conventional sewage treatment plants include biotransformation/biodegradation and/or adsorption on classical adsorbents (e.g., activated carbon) [9]. Previous studies have considered wastewater treatment plants (WWTPs) as the main gateways for the release of emerging pollutants into aquatic environments, e.g., Carballa et al. [10] reported around 70% ibuprofen removal by conventional biological treatments in municipal WWTPs, however, classical WWTPs are not specifically designed to remove recalcitrant, low level pharmaceuticals.

Advanced oxidation processes (AOPs) have been considered as a suitable range of technologies to reduce concentration levels and toxicity associated with the pharmaceutical compound—where they are able to deal with the complex stable structures. In particular, electrochemical advanced oxidation processes such as the electro-Fenton process are regarded as an eco-friendly approach based on the formation of strong oxidants with potential to degrade and mineralise organic pollutants.

In the electro-Fenton process, the in situ electrogeneration of hydrogen peroxide under acidic pH via oxygen reduction (Equation (1)), minimises the operating costs through the avoidance of the continuous addition of hydrogen peroxide to the bulk solution (as is common in the standard Fenton process). The generated hydrogen peroxide reacts with ferrous ion resulting in the production of hydroxyl radicals and ferric ions through Fenton's reaction (Equation (2)). Simultaneously, the continuous regeneration of ferrous ions from ferric ions occurs on the cathode (Equation (3)) ensuring an adequate catalytic concentration in the aqueous phase, with the associated reduction in free radical scavenging (Equation (4)):



Furthermore, water molecules in the bulk solution may be oxidised to oxygen at the anode subsequently generating additional hydrogen peroxide (via Equation (5)). By using anode materials with high over potential such as platinum and boron-doped diamond (BDD), hydroxyl radicals may be formed on the anodes surface according to Equation (6) [11]:



Table 1. List of common pharmaceuticals mineralised by electro-Fenton processes.

Pharmaceutical.	Class	Group	WS (mg/mL)	PNEC ^a (g/L)	Pharmaceutical	Class	Group	WS (mg/mL)	PNEC ^a (µg/L)
Acebutolol	β-blocker	Cardioselective	0.259	n.a.	Amoxicillin	Antibiotic	Penicillin	3.43	489.53
Atenolol	β-blocker	Cardioselective	13.3	n.a.	Cephalexin	Antibiotic	Cephalosporin	10	228.73
Cephazolin	Antibiotic	Cephalosporin	0.21	2432.48	Ciprofloxacin	Antibiotic	Fluoroquinone	30	77.02
Chloramphenicol	Antibiotic	Chloramphenicol	2.5	186.59	Diclofenac	NSAIDs	Acid acetic derivatives	0.002	11.32
Enoxacin	Antibiotic	Fluoroquinone	3.43	94.93	Gemfibrozil	NSAIDs	Fibric acid derivatives	0.011	223.09
Gentamycin	Antibiotic	Aminoglycosides	100	n.a.	Ibuprofen	NSAIDs	Propionic acid derivatives	0.021	25.43
Levofloxacin	Antibiotic	Fluoroquinone	40.4	57.10	Metronidazole	Antibiotic	Nitroimidazole	5.92	13.00
Nafcillin	Antibiotic	Penicillin	0.017	n.a.	Naproxen	NSAIDs	Propionic acid derivatives	0.015	10.36
Ofloxacin	Antibiotic	Fluoroquinone	25	57.10	Propranolol	β-blocker	Cardioselective	0.061	13.01
Sulfamethazine	Antibiotic	Sulfonamides	1.5	n.a.	Sulfamethizole	Antibiotic	Sulfonamides	0.10	n.a.
Sulfamethoxazole	Antibiotic	Sulfonamides	0.61	164.58	Tetracycline	Antibiotic	Tetracyclines	3.87	460.38

NSAIDs: nonsteroidal anti-inflammatory drugs, WS: water solubility (values obtained from PubChem@database), PNEC: predicted no-effect concentrations using Daphnia Magna model (µg/L). ^a [8].

According to the literature, the electro-Fenton mechanism depends considerably on the solution pH [12]. Under acidic conditions ($\text{pH} < 4.5$), the limiting step in the electro-Fenton process corresponds to the iron redox cycle, determined by the solubility of the catalyst. H_2O_2 activation by the dissolved iron source at neutral and alkaline conditions is negligible and thus, maintaining a soluble catalyst determines the production rate of hydroxyl radicals.

Despite research demonstrating high removal and mineralisation percentages with a wide range of pharmaceutical target pollutants, the electro-Fenton process suffers from multiple operational limitations, mainly attributed to the homogeneous process. These include a narrow working pH, difficult catalyst reusability and additional pollution by soluble salts in the effluent.

To advance the field and develop industrially scalable technology, the search of new heterogeneous catalysts applied to electro-Fenton processes has gained attention from the scientific research community with a considerable number of Scopus® indexed scientific publications over recent years. The number of relevant articles, reviews, report, data studies and books including the keyword “heterogeneous catalyst” related to water purification using electro-Fenton process has increased exponentially over the past 5 years (Figure 1a), with research on antibiotic removal gaining more interest than the other classes of pharmaceutical compounds (Figure 1b).

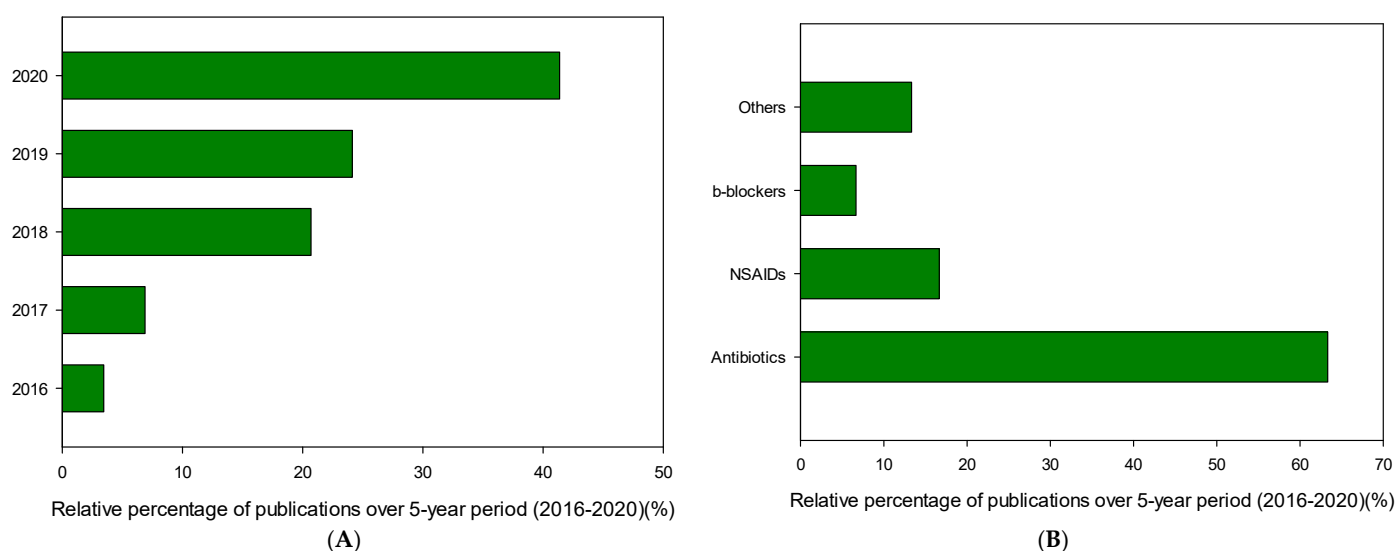


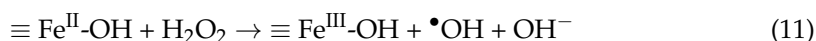
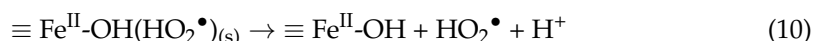
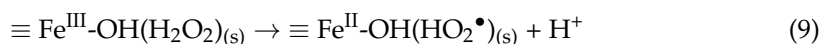
Figure 1. Relative percentage (%) of the total heterogeneous electro-Fenton process publications over the 5-year period (2016–2020) for pharmaceutical removal from the aqueous phase as a function of the published year (A) and class of pharmaceuticals (B) (Source: Scopus®).

The research reported in this review article specifically covers this period of intense growth (2016–2020), focusing on pharmaceutical removal by heterogeneous electro-Fenton process. The basic fundamentals and characteristics of heterogeneous electro-Fenton process have been described to aid in the understand of the key role played by reactive oxygen species produced by the process. Furthermore, an analysis of critical process parameters underpinning heterogeneous catalysts for pharmaceutical removal has been detailed. Finally, the case study example is included, detailing the application of heterogeneous electro-Fenton process for the removal of common pharmaceuticals from aqueous solution.

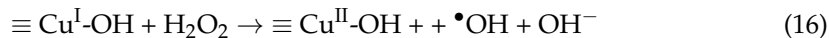
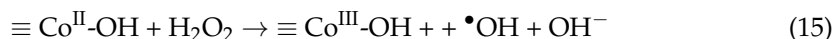
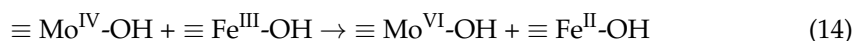
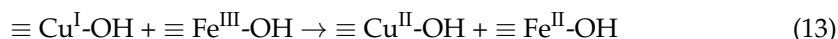
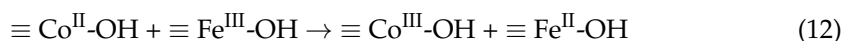
2. Fundamentals of Heterogeneous Electro-Fenton Process

To date, the Haber–Weiss cycle mechanism has been considered the primary reaction mechanism for heterogeneous electro-Fenton process [12]. Hydroxyl radical generation on the catalyst surface begins by the interaction of H_2O_2 and iron species such as $\equiv\text{Fe}^{\text{III}}\text{-OH}$ and $\equiv\text{Fe}^{\text{II}}\text{-OH}$ (Equation (7)) resulting in a $\equiv\text{Fe}^{\text{III}}\text{-OH}(\text{H}_2\text{O}_2)_{(\text{s})}$ formation (Equation (8))

at the cathode. This complex may be subjected to reversible ground-state electron transfer (Equation (9)) and further deactivation (Equation (10)) to generate $\equiv \text{Fe}^{\text{II}}\text{-OH}$ and HO_2^\bullet . Subsequently, $\equiv \text{Fe}^{\text{II}}\text{-OH}$ catalyses H_2O_2 decomposition to form hydroxyl radicals (Equation (11)) which subsequently attack pollutant species, theoretically resulting in the complete mineralisation of the parent compound and intermediates to CO_2 and H_2O [12,13]:



Nowadays, metal sulphides (MoS_2 , WS_2 , Cr_2S_3 , CoS_2 , PbS or ZnS) are widely used as excellent co-catalysts to enhance hydroxyl radical production. The unsaturated sulphur atoms on the metal sulphides surface can capture protons to generate H_2S and release metallic active sites with reductive properties. Thus, co-catalysts facilitate the continuous production of $\equiv \text{Fe}^{\text{II}}\text{-OH}$ and hydroxyl radical generation (Equations (12)–(17)) [14]:

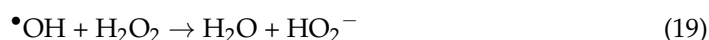


3. Experimental Variables and Parameters of Heterogeneous Electro-Fenton Process

The performance of the electro-Fenton process depends on the several experimental variables such as cell configuration, electrodes material, solution pH, air flow (oxygen supply), and both catalyst and pollutant concentrations. Of these experimental variables, catalyst concentration, applied current density and pH have received the most attention with optimisation reaching maximum efficiency in terms of the chemical oxygen demand (COD) and total organic carbon (TOC) removal. However, relevant parameters related to oxidation efficiency and energy consumption must also be analysed to evaluate the electro-Fenton process performance. To this end, multiple iterative electro-Fenton experimental runs are often carried out by varying exclusively one influencing variable. In general, concentration–time profiles are produced, which exhibit exponential decay with increased treatment with rate constants generated via pseudo-first order kinetics.

3.1. Effect of Catalyst Concentration

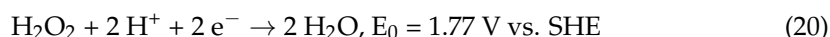
The degradation rate classically increases as a function of catalyst loading reaching a plateau; however, additional catalyst concentration creates the negative effects decreasing removal efficiency. This is likely due to the presence of scavenging reactions between hydroxyl radicals and an excess of iron released into the bulk solution (Equations (18) and (19)) [15,16]:



Furthermore, the inclusion of excessive catalyst promotes aggregation within the bulk solution which results in a decrease in catalyst active surface area and an associated reduction in degradation [15].

3.2. Influence of Applied Current Intensity

Applied current intensity has been considered responsible for the regulation of hydroxyl radical generation (Equations (1) and (3)), and M(OH) production (Equation (7)) [17]. At low current densities, H₂O₂ electrogeneration takes place under conditions of controlled electron transfer. Therefore, increasing the current enhances charge distribution through the cathode, leading to an increase in hydroxyl radical concentration within the solution. Nevertheless, the excessive current can promote side reactions such as H₂O₂ decomposition (Equation (20)) and a reduction of as-generated protons to hydrogen gas (Equation (21)) [15,18]:



3.3. Solution pH Effect

pH of the solution represents a key role in the degradation and subsequent mineralisation of organic pollutants via heterogenous electro-Fenton process in the presence of solid catalysts [19], primarily due to catalyst surface charge and dissolution characteristics. The use of a heterogeneous catalyst allows operation at circumneutral and alkaline conditions with slow degradation efficiency noted over pH 4.5 as a result of the H₂O₂ decomposition into H₂O and O₂ [16]. pH variations have been associated with the continuous hydrolysis of catalyst ions such as iron and copper, leading to enhanced pollutant removal mediated by free radicals oxidation [20].

3.4. Oxidation Efficiency and Energy Consumption

From total organic carbon (TOC) measurements, mineralisation current efficiency (MCE) for an electrolysed solution may be estimated using Equation (22)) [21]:

$$\text{MCE (\%)} = (n \times F \times \Delta(\text{TOC})_{\text{exp}}) / (4.32 \times 10^7 \times m \times I \times t) \quad (22)$$

where *n* is the number of electrons consumed per molecule mineralised, *F* is Faraday's constant (96,500 C/mol), *V* is the volume (L), $\Delta(\text{TOC})_{\text{exp}}$ is the experimental TOC decay (mg/L), 4.32×10^7 a conversion factor, *m* is the number of carbon atoms within the molecule and *I* is the applied total current (A). The number of electrons (*n*) exchanged per each pollutant molecule is estimated as a function of total mineralisation to carbon dioxide and inorganic ions.

Electrical energy consumption has been considered as the main operational cost for electrochemical technologies [22,23]. When operating at a constant applied current, the energy consumption per unit volume (EC) and unit TOC mass (EC_{TOC}) are calculated as described in Equations (23) and (24), respectively:

$$E_C (\text{kWh/m}^3) = (E_{\text{cell}} \times I \times t) / V \quad (23)$$

$$E_{\text{TOC}} (\text{kWh/g}_{\text{TOC}}) = (E_{\text{cell}} \times I \times t) / (\Delta(\text{TOC})_{\text{exp}} \times V) \quad (24)$$

where *E_{cell}* is the average potential difference (V), *I* is the applied current intensity (A), *V* the volume (L), *t* the electrolysis time (h) and $\Delta(\text{TOC})_{\text{exp}}$ the experimental TOC decay (mg/L).

The potential generation of more toxic organic compounds than the parent pollutant via the electro-Fenton process represents one of the main drawbacks associated with the use of this technology. Thus, adequate parameters such as the average oxidation state (AOS) and carbon oxidation state (COS) are often selected to analyse the proportion of biodegradable organic compounds present into the aqueous solution. These parameters are derived based upon TOC and COD evolution and described by Equations (25) and (26) [24,25]:

$$\text{AOS} = 4 \times (\text{TOC}-\text{COD}) / \text{TOC} \quad (25)$$

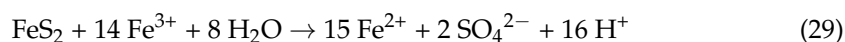
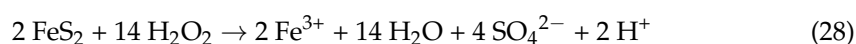
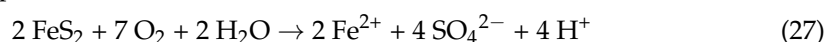
$$\text{COS} = 4 \times (\text{TOC}_0 - \text{COD}) / \text{TOC}_0 \quad (26)$$

where TOC_0 is the initial concentration of total organic carbon (mmol C/L), TOC the total organic carbon at time t (mmol C/L) and COD the chemical oxygen demand (mmol O_2/L) at time t . COS represents the carbon oxidation efficiency considering the carbon removed from the solution as gaseous CO_2 . Regarding AOS , the maximum value +4 corresponds to the highest oxidised state of carbon, CO_2 , with the minimum value -4 corresponding to the most reduced state of carbon, CH_4 .

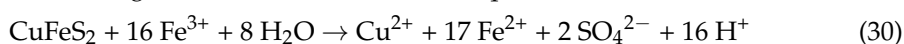
4. Heterogeneous Catalysts

Apart from the experimental variables mentioned above which affect the efficiency of heterogeneous electro-Fenton process, mass transfer limitations are considered an important drawback of these catalytic systems [26]. The catalytic reaction takes place after the diffusion step towards the catalyst particles (external/film diffusion) and through the pore within the particle (internal diffusion). As a consequence, the search for a novel heterogeneous catalyst able to reduce the mass transfer limitations represents a challenging milestone on the research community.

Many publications have demonstrated the potential of natural iron minerals including hematite, goethite and magnetite, to catalyse H_2O_2 decomposition to hydroxyl radicals (Figure 2A) [26,27]. Recently, Barhoumi et al. [27] assessed the viability of pyrite as a heterogeneous iron source for antibiotic degradation. At optimum conditions, around 96% mineralisation was achieved after 8 h treatment, suggesting pyrite as an adequate solid catalyst for the electro-Fenton process. The efficiency of the pyrite-based electro-Fenton process was associated with the self-regulator of iron dosage and pH in the system according to the Equations (27)–(29):



Additionally, the use of chalcopyrite has been evaluated by Droguett et al. (2020) for cephalexin degradation; this mineral possesses the same catalytic behaviour as pyrite, again acting as a self-regulator in the bulk solution (Equation (30)):



Natural iron-based composites have been investigated for heterogeneous electro-Fenton process targeting removal of pharmaceuticals [28]. Iron nanoparticles have high reactivity in water, leading to high surface energy, oxidation and passivation processes. To overcome these drawbacks, transition metals, such as copper, have been incorporated with iron nanoparticles, resulting in the development of bimetallic nanoparticle composites. The synergetic effect of the physicochemical properties of each metal enhances both the degradation activity and stability, providing efficient electron transfer. Campos et al. [29] evaluated the removal of nafcillin from aqueous solution using iron and copper monometallic and bimetallic nanoparticles as electro-Fenton catalysts. They used bimetallic nanoparticles as the catalyst to overcome the limitations associated with the use of ferromagnetic materials. XRD and SEM characterisation confirmed the presence of metallic Fe, Cu and FeOOH in addition to a range of morphologies attributed to formation of metal oxides. In line with the theory, the use of bimetallic nanoparticles catalysed the total removal of the antibiotic with lower treatment time than either monometallic nanoparticle. However, during catalyst reuse trials, the pollutant removal percentage decreased by up to 77% following three consecutive cycles due to the formation of oxides (FeO , Fe_2O_3 and CuFe_2O_4) on the nanoparticle surface. Similar results were obtained by Ghasemi et al. [15], who synthesised nano-layered double hydroxide (NLDH) compounds containing copper and iron, who studied catalytic activity toward gentamicin degradation. Their hydrotalcite structure promoted high surface area and ion-exchange, exhibiting negligible metal leaching and almost full antibiotic degradation under optimal conditions.

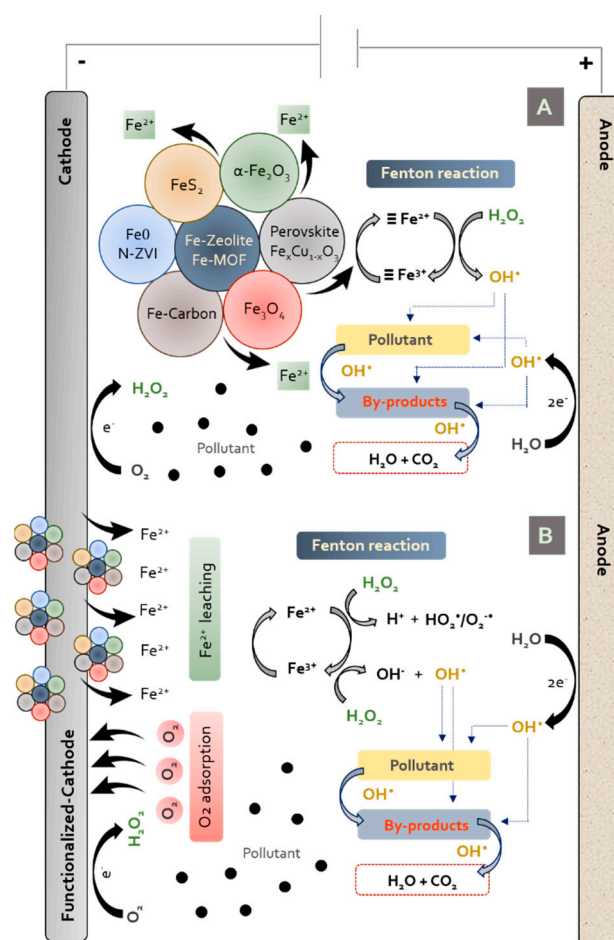


Figure 2. Mechanism of the catalytic activation on the heterogenous electro-Fenton process under acidic conditions: iron solid catalyst (A), iron-functionalised cathodic material (B).

Although the classical-Fenton reaction is based on $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, other transition metals such as copper, chromium, cobalt and manganese may promote H_2O_2 decomposition into $\bullet\text{OH}$ by ‘Fenton-like’ pathways. Copper, as described above, possesses similar redox behaviour to iron operating, under a similar broad pH range to the iron system. Given the importance of the role of the structure, several perovskites containing copper structures have been investigated. $\text{LaCu}_{1-x}\text{M}_x\text{O}_3$ (where $\text{M} = \text{Mn}, \text{Ti}$; $0 \leq x \leq 0.8$) was prepared and tested by Carrasco-Diaz et al. using paracetamol as the chemical probe under mild conditions and circumneutral pH [30]. Manganese and titanium were selected as the B position metals owing to their good activity in Fenton-like reactions. Based on their results, copper exhibited higher redox activity, whereas titanium and manganese were not responsible for the enhancement of antibiotic degradation. Negligible metal leaching and high metal stability within the network structure confirm this material as a promising alternative catalyst.

Novel composites containing iron species have been synthesised [31]. Fe_2O_3 -modified kaolin was proposed by Özcan et al. [31] as a promising alternative for enoxacin degradation from aqueous environments. The use of clays such as kaolin and perlite has been widely applied primarily as catalyst supports due to their low cost, high adsorption ability and eco-friendly structure [32]. Carbonaceous materials have also been recently used as immobilisation substrates to enhance catalytic activity, stability and reusability. The incorporation of core-shell structured catalysts, with a transition metal nanoparticle core and a porous carbon shell, allows for enhanced catalytic properties whilst minimising catalyst agglomeration. $\text{Fe}/\text{Fe}_3\text{C}@\text{PC}$ core-shell structured materials were synthesised by Du et al. [33] and tested for the degradation of sulfamethazine solutions. The aid with

sustainability and catalyst reuse, this catalyst can be magnetically captured and further recovered via a thermal treatment in a H_2 atmosphere. As was expected, $Fe/Fe_3C@PC$ exhibited enhanced performance compared to the pristine iron oxides, given the synergetic effect between Fe/Fe_3C and PC, again demonstrating the potential in nano-engineering to improve electro-Fenton catalyst form and function.

Graphene and its derivatives have also been considered suitable supporting materials for catalyst immobilisation due to their high thermal and electrical conductivity, strong mechanical and chemical stability, extremely high specific area and relatively simple synthesis methods from graphite (by chemical oxidation–exfoliation–reduction procedures and mechanical means). The oxygenated functional groups located on the edges (carbonyl and carboxyl) and basal plane (epoxides and hydroxyl) act as a nucleation site for metal ions to produce graphene-based nanocomposites [34].

5. Heterogeneous Electro-Fenton Process with Iron Functionalised-Cathode

Further work in the discipline of nano-engineering includes the use of three-dimensional electrodes in order to enhance the mass transfer and conductivity into the electro-Fenton system [35]. This innovative electrochemical system provided an enhanced effective contact area and numerous micro-electrolysis cells; therefore, the electrochemical reactions take place on the main electrode surface and the particle electrode surface. The cathodic-modification via the addition of iron and/or transition metal oxides, incorporates dual functionality, as both a counter electrode and an iron source, and may be carried out by the immobilisation of an iron source and/or through the chemical modification of the carbonaceous material.

Although these systems show high pollutant removal effectiveness, some operational limitations may hinder their widespread use in water purification, such as low current efficiency and narrow operating pH range. Mohammadi et al. [35] studied $Fe-Ni$ foam particles on three-dimensional electrodes for NSAIDs removal using $Ti-PbO_2$ and graphite felt as the anode and cathode, respectively. This system achieved nearly a two-fold increase in the removal percentage when compared to a corresponding 2D electro-Fenton system. The authors attributed the increased rate to a higher concentration of radical species generation because the Ni -foam electrode may activate molecular oxygen to produce single oxygen. Recently, Luo et al. [20] proposed a Cu -doped $Fe@Fe_2O_3$ core-shell nanoparticle (CFF) system loaded on a nickel-based foam as the cathode and examined efficiency for tetracycline degradation. XRD and XPS experiments allowed the determination of the catalyst composition showing an Fe/Cu nanoparticle core and an external layer-shell of metal oxides (Fe_2O_3 , Cu_2O and CuO). Catalytic performance was reported to decline with increasing Cu content due to a reduction in active Fe^0 sites. For optimal Fe/Cu loadings, catalyst reusability was demonstrated over six successive runs with negligible iron leaching was observed.

The development of iron-functionalised cathodic materials (Figure 2B), such as active carbon/fibre, carbon felt, graphite felt and carbon aerogels, has recently received significant attention. In particular, Mi et al. [36] investigated the electrocatalytic performance of mesoporous $Mn_xCo_{3-x}O_4$ nanoparticle modified carbon felt as an electro-Fenton cathode. Higher ciprofloxacin degradation rates were achieved as a result of increasing electron transfer and the redox reactivity. This was associated with the synergetic effect of embedded cobalt and manganese within the mesoporous matrix and promotion of more accessible active sites. The reusability of the modified cathode was evaluated via five successive cycles with minimal ion leaching measured (below 3.5 ppm). Similarly, Yang et al. [13] prepared heterogeneous $Fe^{II}Fe^{III}$ -layered double hydroxide ($Fe^{II}Fe^{III}LDH$) modified carbon felt by an in situ solvothermal method for ofloxacin removal. Hydroxyl radical mediated mineralisation of ofloxacin was attributed to the formation of $BDD(*OH)$ via the electrochemical process and surface iron oxide catalysis through the $Fe^{II}Fe^{III}$ cycle. These results support the work of Ganiyu et al. [37], who evaluated $Fe^{II}Fe^{III}LDH$ modified carbon felt as cathode for sulfamethoxazole degradation. Nsubuga et al. [38] synthesised a $Cu-B-Fe$

modified-graphite electrode and trailed the approach for the degradation of two β -blockers (atenolol and propranolol). As was previously observed, they also concluded that the bimetallic catalysts possess higher stability than monometallic electrode materials and additionally benefited from good thermal and recycling stability and conductivity. The use of magnetic single walled carbon nanotubes (MWCNTs) as a carrier for the electrocatalyst was reported by Pourzamani et al. [39]. These materials possess a high specific surface area, notable chemical and mechanical stability and high electrical conductivity. Comparative analysis between several electrocatalytic degradation technologies demonstrated MWCNTs to have a high efficiency and enhanced energy-saving than three-dimensional electrode systems, likely due to the significantly greater surface area of the MWCNTs and the strong interaction between Fe_2O_3 and MWCNTs.

6. Application of Electro-Fenton Process for the Removal of Pharmaceutical Compounds

Given the interest in new electro-Fenton processes for the remediation of low level, persistent, recalcitrant emerging water pollutants, and in particular pharmaceutical compounds, antibiotics, β -blockers and nonsteroidal anti-inflammatory drugs (NSAIDs) have been prominently featured in published research over last five years, as shown in the comprehensive summary (Tables 2 and 3). In this section, several investigations have been discussed based on the type of pharmaceutical compounds. Although the mineralisation pathways of these compounds depend on the molecular structure of the target pollutant and operational conditions, common oxidation steps take place on the degradation/mineralisation process by electro-Fenton-based processes. Succinctly, hydroxylation reactions on the side chain occur by the attack of hydroxyl radicals and hydroxylated cyclic hydrocarbons were obtained by the cleavage of C-S, N=N, N-N, S-N, C-N, C-C and C=C bonds. For instance, the C=C bond on the tetracycline molecule has been reported as the most reactive position for the hydroxyl radical attack leading to the production of the major intermediate [13]. Further hydroxylation, decarboxylation, demethylation, deamination, desulfonation and dichlorination reactions, as well as ring opening steps lead to the formation of short-chain carboxylic acids reported as end-products prior to the total mineralisation up to carbon dioxide, water and inorganic ions.

Table 2. Summary of some relevant studies on heterogeneous electro-Fenton systems.

Pharmaceutical (Concentration)	Catalyst (Concentration)	Anode/Cathode	Operational Conditions	Removal and TOC Decay	References
Sulfamethazine (0.2 mM)	Pyrite (2 g/L)	BDD/CF	0.05 M Na ₂ SO ₄ , pH:3, AFR: 1 L/min, I = 300 mA	100% removal (40 min)	[40]
Tetracycline (0.2 mM)	Pyrite (2 g/L)	BDD/CF	0.05 M Na ₂ SO ₄ , pH:3, AFR: 1 L/min, I = 300 mA	100% removal (20 min) 96% TOC decay (480 min)	[27]
Tetracycline (0.2 mM)	Chalcopyrite (1 g/L)	BDD/CF	0.05 M Na ₂ SO ₄ , pH:5.94, AFR: 0.6 L/min, I = 300 mA	100% removal (7 min) 85% TOC decay (120 min)	[17]
Cephalexin (50 mg/L)	Chalcopyrite (1 g/L)	IrO ₂ /air diffusion cathode	0.05 M Na ₂ SO ₄ , pH:3, AFR: 0.6 L/min, I = 125 mA	94% removal (15 min) 44% TOC decay (300 min)	[16]
Metronidazole (70 mg/L)	Nano-Fe ₂ O ₃ (1 g/L)	Pt sheet/GF	0.05 M Na ₂ SO ₄ , pH:3, I = 200 mA	92.3% removal (30 min)	[41]
Amoxicillin (20 mg/L)	Nano-Fe ₂ O ₃ (1 g/L)	Pt sheet/GF	0.01 M Na ₂ SO ₄ , pH:3, AFR: 1 L/min, I = 300 mA	98.2% removal (60 min)	[42]
Diclofenac (140 mg/L)	Fe ₂ O ₃ -modified chitosan (20 g/L)	BDD/CF	0.01 M Na ₂ SO ₄ , pH:6, AFR: 1 L/min, I = 300 mA	95% removal (120 min) 74.4% TOC decay (8 h)	[43]
Sulfamethizole (25 mg/L)	FeCl ₃ -modified perlite (n.a.)	BDD/CF	0.01 M Na ₂ SO ₄ , pH:6, AFR: 1 L/min, I = 300 mA	100% removal (15 min) 65% TOC decay (120 min)	[32]
Enoxacin (0.25 mM)	Fe ₂ O ₃ -modified kaolin (1.7 g/L)	BDD/CF	0.05 M Na ₂ SO ₄ , pH:3, AFR: 1 L/min, I = 300 mA	100% removal (15 min) 98% TOC decay (420 min)	[31]
Diclofenac (10 mg/L)	MSWCNTs-FeCl ₂ (80 mg/L)	Ti-RuO ₂ /GF	0.05 M Na ₂ SO ₄ , pH:5, AFR: 1 mL/min, d = 20 mA/cm ²	97.8% removal (120 min) 71% TOC decay (120 min)	[44]
Gentamicin (20 mg/L)	Cu-Fe-NLDH (1.25 g/L)	Pt sheet/graphite plate	0.05 M Na ₂ SO ₄ , pH:6, AFR: 10 L/h, I = 400 mA	91.3% removal (100 min)	[15]
Nafcillin (36 mg/L)	Fe/Cu bimetallic nanoparticles (1 g/L)	BDD/carbon-PTFE air diffusion	0.05 M Na ₂ SO ₄ , pH:7, d = 5 mA/cm ²	100% removal (7 min)	[29]
Chloramphenicol (80 mg/L)	Fe ₃ O ₄ -GO (0.5 g/L)	Pt gauze/CF	0.05 M Na ₂ SO ₄ , pH:3, AFR: 10 L/h, I = 300 mA	100% removal (45 min) 86% TOC decay (300 min)	[45]
Metronidazole (80 mg/L)	Fe ₃ O ₄ -GO (0.5 g/L)	Pt gauze/CF	0.05 M Na ₂ SO ₄ , pH:3, AFR: 10 L/h, I = 300 mA	100% removal (15 min) 73% TOC decay (300 min)	[45]

Table 2. Cont.

Pharmaceutical (Concentration)	Catalyst (Concentration)	Anode/Cathode	Operational Conditions	Removal and TOC Decay	References
Propranolol/acebutolol (200 ng/mL each)	Fe-C (119 mg/L)	BDD/air diffusion cathode	0.05 M Na ₂ SO ₄ , pH:7, d = 75 mA/cm ²	100% removal (15 min)	[46]
Diclofenac (50 mg/L)	Pyrite (8 g/L)	Pt mesh/air diffusion cathode	0.05 M Na ₂ SO ₄ , pH:7, AFR: 0.4 L/min, d = 31.84 mA/cm ²	97.8% removal (8 min) 85% TOC decay (180 min)	[47]
Gemfibrozil (10 mg/L)	nano-ZVI@C-N (0.2 g/L)	Ti-IrO ₂ /air diffusion cathode	0.05 M Na ₂ SO ₄ , pH:6, AFR: 1 L/min, I = 300 mA	95% removal (60 min)	[48]

TOC: total organic carbon, BDD: boron-doped diamond, CF: carbon felt, GF: graphite felt, MSWCNTs: magnetic single walled carbon nanotubes, AFR: air flow rate, GO: graphene oxide, PTFE: polytetrafluoroethylene.

Table 3. Summary of some relevant studies on heterogeneous electro-Fenton systems using iron-functionalised cathode.

Pharmaceutical (Concentration)	Catalyst (Concentration)	Anode/Cathode	Operational Conditions	Removal and TOC Decay	References
Ibuprofen (10 mg/L)	Ferric citrate	Ti-RuO ₂ /Cit-Fe-ACFs	0.05 M Na ₂ SO ₄ , pH: 6.8, AFR: 0.1 L/min, d = 5 mA/cm ²	97% removal (120 min)	[49]
Sulfamethazine (10 mg/L)	Fe/Fe ₃ C@CP (0.05 g/L)	Ti-RuO ₂ /CB-CF	0.05 M Na ₂ SO ₄ , pH: 3, I = 25 mA	99% removal (30 min)	[33]
Levofloxacin (80 mg/L)	Fe/Fe ₃ C@CP (0.05 g/L)	Ti-RuO ₂ /CB-CF	0.05 M Na ₂ SO ₄ , pH: 3, I = 25 mA	97% removal (60 min)	[33]
Ibuprofen (4 mg/L)	Fe-NFP	Ti-PbO ₂ /GF	pH: 6.3, d = 15.77 mA/cm ²	98% removal (38 min)	[35]
Naproxen (4 mg/L)	Fe-NFP	Ti-PbO ₂ /GF	pH: 6.24, d = 18.91 mA/cm ²	93% removal (38 min)	[35]
Diclofenac (6.71 mg/L)	MSWCNTs-Fe ₃ O ₄ (58.33 mg/L)	Ti-RuO ₂ /MSWCNTs-Fe ₃ O ₄ -GF	0.05 M Na ₂ SO ₄ , pH: 5.56, AFR: 1 mL/min, d = 19.74 mA/cm ²	98% removal (83 min)	[39]
Ciprofloxacin (0.1 mM)	Fe ²⁺ (0.1 mM)/MnCo ₂ O ₄	Pt plate/MnCo ₂ O ₄ -CF	0.05 M Na ₂ SO ₄ , pH: 3, AFR: 10 L/h, I = 300 mA	100% removal (300 min) 75% TOC decay (300 min)	[36]

Table 3. Cont.

Pharmaceutical (Concentration)	Catalyst (Concentration)	Anode/Cathode	Operational Conditions	Removal and TOC Decay	References
Sulfamethazine (10 mg/L)	MoS ₂ (0.02 g/L)/Fe ⁰ (0.224 g/L)	Ti–TiO ₂ –RuO ₂ /CB–CF	0.05 M Na ₂ SO ₄ , pH: 4, AFR: 50 mL/min, I = 50 mA	100% removal (10 min) 42% TOC decay (60 min)	[14]
Tetracycline (20 mg/L)	Cu-doped Fe@Fe ₂ O ₃ (50% wt. Cu)	Ti–TiO ₂ –RuO ₂ /Cu-doped Fe@Fe ₂ O ₃ –Ni foam	0.05 M Na ₂ SO ₄ , pH: 3, AFR: 0.1 L/min, d = 40 mA/cm ²	98.1% removal (120 min) 89% TOC decay (360 min)	[20]
Atenolol, propranolol (200 ng/L each)	Cu–B–F (n.a.)	BDD/Cu–B–F-modified graphite	0.02 M Na ₂ SO ₄ , pH: 7, I = 100 mA	99.9% removal (10 min)	[38]
Ciprofloxacin (0.1 mM)	Meso-NiMn ₂ O ₄ (n.a.)	Pt plate/meso-NiMn ₂ O ₄ –CF	0.05 M Na ₂ SO ₄ , pH: 3, AFR: 50 mL/min	100% removal (90 min) 75.9% removal (360 min)	[50]
Cefazolin (20 mg/L)	CUFeNLDH–CNTs (1.25 g/L)	Pt sheet/CUFeNLDH–CNTs-graphite	0.02 M Na ₂ SO ₄ , pH: 6, AFR: 10 L/h, I = 300 mA	89.9% removal (100 min) 70.1 COD decay (300 min)	[51]
Sulfamethoxazole (0.2 mM)	Fe ^{II} Fe ^{III} LDH (n.a.)	Ti ₄ O ₇ /Fe ^{II} Fe ^{III} LDH–CF	0.05 M Na ₂ SO ₄ , pH: 3, AFR: 1 L/min, d = 7.5 mA/cm ²	100% removal (40 min) 97% TOC decay (480 min)	[37]
Ofloxacin (0.1 mM)	Fe ^{II} Fe ^{III} LDH (n.a.)	BDD/Fe ^{II} Fe ^{III} LDH–CF	0.05 M Na ₂ SO ₄ , pH: 7, AFR: 0.75 L/min, d = 12.5 mA/cm ²	100% removal (30 min) 100% TOC decay (480 min)	[13]

TOC: total organic carbon, CF: carbon felt, GF: graphite felt, MSWCNTs: magnetic single walled carbon nanotubes, CB–CF: carbon black modified carbon felt, NLDH: nano-layered double hydroxide; AFR: air flow rate, CNTs: carbon nanotubes, NFP: nickel foam particles.

6.1. Antibiotics

The widespread overuse of antibiotics, mainly in primary care, and poor removal efficiency in WWTP results in trace level antibiotics being considered a significant hazard to both environment and human health. Tetracycline, used to control the urinary tract, respiratory tract and the intestinal infections has been detected in natural water at concentrations up to 1.4 µg/L [27]; likewise, ciprofloxacin, widely used against a range of bacterial infections has been detected at concentrations ranging from 0.407 nmol/L in Europe to 20,000 nmol/L in Asia [52].

Fluoroquinones including ciprofloxacin, levofloxacin or ofloxacin have been detected in aquatic ecosystems and drinking water at concentrations around ng/L [36]. Mi et al. [36] examined the effectiveness of carbon felt modified with $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ mesoporous nanoparticles for ciprofloxacin removal. SEM images showed the successful deposition of MnCo_2O_4 nanoparticles on the carbon felt surface and uniform distribution of the elements within the nanoparticles. Based on cyclic voltammetry analysis, the authors concluded that higher intrinsic electron transfer promoted increased redox reaction capacity due to the synergetic effect between the transition metals in the mesoporous structure. Electron-density distribution analysis showed Co to be present as an electron-rich species (e.g., cobalt oxides) with the uniform nature of the total electron density map suggesting an electron transfer from Co to Mn. Furthermore, the large specific surface area, notable H_2O_2 yield and excellent hydroxyl radical production rate promoted high levels of ciprofloxacin removal. Similar results were obtained by Du et al. [33], who degraded levofloxacin using Fe/Fe₃C and graphitised porous carbon shell systems. A particular benefit of this system is the inherent magnetic property which permits the post-treatment separation of the particles, recycling and reuse. From their results, the saturation magnetisation decreased from 70.1 up to 49.5 emu/g after use due to leaching of iron and the deposition of iron oxides on the particles during pollutant degradation experiments.

Yang et al. [13] also analysed supported catalysis, investigating the performance of Fe^{II}Fe^{III}-LHD modified carbon felt cathodes for ofloxacin removal at near neutral pH. Complete TOC abatement was attained after a 480 min treatment in a system applying a current density of 9.37 mA/cm². Notable removal efficiency was observed at pH 7 as a result of the surface catalysed process at the solid–liquid interface, preventing the precipitation of iron hydroxide. The authors calculated the electroactive surface of the modified cathode and unmodified materials to determine the rate of the electrochemical reactions on the cathode, using cyclic voltammetry runs in a 10 mM $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ solution with the electroactive surface estimated by Randles–Sevcik equation (Equation (31)):

$$I_p = 2.69 \times 10^5 \times A \times D^{1/2} \times n^{1/2} \times \nu^{1/2} \times C \quad (31)$$

where I_p is the maximum peak current (A), n is the number of electrons involved in the redox reaction ($n = 1$), A is the area of the electrode (cm²), D is the diffusion coefficient of the molecule in the solution (7.6×10^{-6} cm²/s), C is the concentration of the standard molecule in the bulk solution (10^{-5} mol/mL) and ν is the scan rate (0.01 V/s).

Accordingly, the electroactive surface area was calculated to be 42 cm² for the raw carbon felt and 127 cm² with the Fe^{II}Fe^{III} LDH-modified CF, thus, a three-fold improvement in surface area resulted in the increased performance of the electrocatalytic reactions on the cathode. Consequently, the increasing current density impacted on the economic parameters (MCE and EC) and parallel reactions were observed, such as H₂ evolution on the cathode and O₂ formation on the anode. Positive outcomes included negligible iron leaching demonstrating catalyst stability at circumneutral pH.

Tetracyclines represent another common class of antibiotics, with many studies targeting their removal. The use of iron-based minerals such as pyrite and chalcopyrite was investigated by Oturan and Brillas groups [17,27] achieving a 100% removal of tetracycline (C₂₂H₂₄N₂O₈) in less than 20 min. Under similar operational conditions, the use of chalcopyrite as a catalyst exhibited a higher degree of mineralisation due to the contribution of copper ions. Given the complexity of the tetracycline molecule, the formation of

recalcitrant intermediate products results in significant impact on MCE depletion which is accompanied by an increase in energy consumption per TOC unit. Therefore, the authors suggested a sequential process based on the chalcopyrite/electro-Fenton process followed by conventional treatments for practical applications.

Droguett et al. [16] evaluated the potential use of chalcopyrite as a heterogeneous catalyst to degrade cephalexin achieving a 94% removal of the parent compound within 30 min treatment, however, as can be seen in Table 2, only 44% mineralisation was reached after 300 min due to the emergence of recalcitrant intermediates, such as aromatic compounds and short-chain carboxylic acids, the latter leading to the formation of stable organo-iron complexes, which cannot be degraded by hydroxyl radicals. Ecotoxicological effects of these by-products of electro-Fenton treatment are often evaluated by classical toxicity studies including *Vibrio fischeri* (Microtox®test), *Daphnia magna* or *Escherichia coli* as model organisms used to assess the general toxicity of the effluent produced from treatment.

Sulphonamide antibiotics, such as sulfamethazine, possess antibacterial activity being widely used for human and veterinary clinical purposes [53,54] and as a consequence has been detected in effluents from the sewage treatment plant and surface water at concentrations ranging from 20 to 1000 ng/L [55]. Many researchers have studied this group of antibiotics over the last five years using a heterogeneous electro-Fenton process (Table 2) [14,33,40]. Tian et al. [14] used commercial MoS₂ as a co-catalyst to develop an efficient MoS₂/Fe⁰ co-catalytic electro-Fenton process. Almost complete sulfamethazine degradation was achieved after 20 min by Fe⁰-electro-Fenton process whereas only 10 min were necessary to achieve the same removal percentage when MoS₂ was introduced as a co-catalyst. These results concur with the data for homogeneous electro-Fenton process, with a higher sulfamethazine removal rate evident in the presence of the co-catalyst. The effect was attributed to the acceleration of the Fe³⁺/Fe²⁺ reactions (Equation (14)) with an associated increase in the generation of hydroxyl radicals (Equation (17)) experimentally demonstrated. Similar sulfamethazine degradation studies were also reported by Barhoumi et al. [40] and Du et al. [33].

The degradation of sulfamethizole was undertaken by Puga et al. [32], who used electro-Fenton process in ultrapure water and real treated wastewater spiked with the pollutant (final concentration around 25 mg/L) under a continuous flow-system. The authors assumed a first-order kinetic model for mineralisation data reporting kinetic rate constants around 0.27 and 0.15 1/h for ultrapure and real water, respectively, demonstrating the challenge of working with real effluent. Campos et al. [29] also observed this effect, reporting the influence of feed water composition on radical scavenging reactions coupled with mass transfer limitations due to the presence of organic matter. Under optimal conditions, nafcillin was completely removed from the slaughterhouse effluent after 15 min treatment, demonstrating efficacy in a very challenging wastewater matrix. A range of other works report similar behaviour [49,56] within limited TOC reduction observed in effluent-based experiments.

β-lactam antibiotics, including penicillin, are a group of compounds commonly used to treat a wide range of bacterial infections. Amoxicillin, a well-known broad-spectrum β-lactam is non-biodegradable and detected in groundwater, surface waters, hospital effluents and industrial wastewater streams at concentrations ranging from sub-ng/L up to 87.5 g/L [57]. Their toxic and recalcitrant character hinders removal by conventional biological treatments and thus, the use of AOPs including Fenton-based processes have been investigated for amoxicillin degradation [58–60]. Kalantary et al. [42] studied the performance of a heterogeneous electro-Fenton process using nano-Fe₃O₄ modified-carbon felt cathodes which increased the H₂O₂ yield 5.2-fold without aeration, demonstrating promise for the application of the electro-Fenton process at low oxygen levels. Optimisation of the process was carried out to ensure the minimum applied current and as such deliver an economic and energy favourable process, with the authors reporting a tenfold decrease in terms of energetic consumption (Equation (23)) within a minimal impact on process effectiveness (9% decrease from optimal efficiency).

Chloramphenicol, a broad-spectrum antibiotic used in veterinary medicine, and although banned in the European Union and many other countries due to its harmful effects detected in humans, has been detected in food products arriving from Asia [61]. Several authors have reported the applicability of AOPs to degrade chloramphenicol by hydroxyl and sulphate radical-based mechanisms [62,63]. Görmez et al. [45] reported the potential of GO-Fe₃O₄ as an electro-Fenton catalyst, noting around 80% mineralisation following 300 min treatment under optimal conditions with 16% higher TOC removal when compared to the homogeneous electro-Fenton process. The authors suggested relatively higher activation energy was required for the initiation step of the degradation reaction due to the slow decay of the parent compound. Adsorption studies confirmed that the GO-Fe₂O₃ catalyst contributed directly to the Fenton reaction rather than simply increasing pollutant adsorption.

Nitroimidazole antibiotics, including metronidazole, have been widely used to treat infections caused by anaerobic and protozoan bacteria and have been detected in hospital effluents at concentrations in the range of 1.8–9.4 µg/L [64]. Their low biodegradability, high solubility in water and complex molecular structure hinder their removal by conventional systems [65]. Thus, Rahmatinia and Rahmatinia [41] studied metronidazole removal using nano-Fe₃O₄ as a heterogeneous catalyst reaching 92.2% removal under optimal conditions (70 mg/L initial concentration, pH 3, 200 mA applied current intensity and 3.2 kWh/m³). Similar results have been reported by Görmez et al. [45] with data showing near total degradation after 15 min treatment.

6.2. β -Blockers

Beta adrenergic antagonists (β -blockers) have been widely prescribed to treat cardiac arrhythmias, hypertension and angina, and are commonly detected illegally during antidoping controls [66,67] with transport to the environment reported via effluents from pharmaceuticals plants, hospitals, retirement homes and private households [68].

β -blockers are considered a significant threat to the aquatic organisms due to their high persistence and bioaccumulation in water bodies [69,70]. Nsubuga et al. [46] developed a promising approach for the total elimination of parent propranolol and acebutolol, and their metabolites, using Fe-C nanocomposites synthesised from rice husk. The use of a droplet flow-assisted heterogeneous electro-Fenton reactor ensured synergetic mechanisms of degradation enhancement based on an increased surface area from the droplet chemistry and micro-electrolysis arising from the Fe-C nanocomposite [46]. pH adjustment was not required given the nature of the biogenic iron composites which self-regulate acidity as observed in pyrite and chalcopyrite systems. The authors suggested an electrochemical degradation pathway based on the side chain cleavage to form an amino-diol and hydroxylation of the aromatic ring. Subsequently, Nsubuga et al. [38] analysed copper-boron-ferrite (Cu-B-Fe)-supported graphite electrodes using droplet flow-assisted heterogeneous electro-Fenton process for atenolol and propranolol in hospital effluent. SEM images showed a high dispersion of the Cu, B and Fe on the functionalised cathodic surface. Furthermore, near rectangular shaped cyclic voltammograms of these modified electrodes confirm their high potential to increase electron transfer on the electrode surfaces. Consequently, these electrodes demonstrated excellent activity for in situ H₂O₂ electrogeneration, hydroxyl radical production and catalyst regeneration.

6.3. NSAIDs

NSAIDs are frequently prescribed to treat pain and inflammation associated with arthritis, including acetaminophen (paracetamol), ibuprofen, naproxen and diclofenac; however, few publications have evaluated the production and fate of oxidation by-products and their ecotoxicological effects [71]. Given the routine detection in the aquatic environment [72], the EU Water Framework Directive lists ibuprofen within the first Watch List given regular detection in freshwater and wastewater treatment plant effluents at concentrations over 30 µg/L [73]. Liu et al. [49] reported the use of activated carbon fibre

supported ferric citrate as a modified cathode, achieving 96% ibuprofen degradation at 5 mA/cm² current density after 120 min treatment. High MCE, around 46%, was obtained in comparison with other heterogeneous electro-Fenton processes [31,40]. In addition, this modified cathode is also suitable for use at circumneutral pH similar to Fe₂O₃/kaolin catalysts [31].

Diclofenac is a popular choice of model compound within the scientific community [39,43,44] and has been detected in surface water and groundwater at concentration levels ranging from 0.8 ng/L to 4.4 µg/L [74–76]. Its high solubility at neutral-alkaline conditions and low solubility at pH ≤ pKa (around 4.91) considerably hinder its removal by conventional treatments [77,78]. Rosales et al. [43] have proposed an innovative approach at near neutral pH by using iron chitosan–epichlorohydrin spheres. Previously, Pourzamani et al. [39] reported good removal efficiency using 3D electro-Fenton process based upon multi-walled carbon nanotubes (MWCNTs)–Fe₃O₄ as the electrode. More than 70% degradation was achieved following 120 min, a two-fold increase over heterogeneous electro-Fenton process without cathodic-modification demonstrating the effectiveness of the microelectrodes to increase both indirect and direct oxidation. In addition, less H₂O₂ accumulation was detected in the bulk solution as a result of rapid decomposition to hydroxyl radicals [79]. Similar enhancement was reported by Sadeghi et al. [44] using Fe–MWCNTs as the heterogeneous catalyst.

7. Photoelectro-Fenton Process

The effectiveness of the heterogeneous electro-Fenton process may be enhanced through combination with other technologies. Hybrid processes integrated into systems, sequential alternative and successive treatments have been proposed with many examples reporting total pollutant removal from wastewater (summarised in Table 4). Photoelectro-Fenton (PEF) process represents an ‘upgrade’ to electro-Fenton via the simultaneous exposure of the solution to UV and/or visible radiation [80] (Figure 3).

Table 4. Summary of some relevant studies on heterogeneous photoelectro-Fenton systems.

Pharmaceutical (Concentration)	Catalyst (Concentration)	Anode/Cathode	Operational Conditions	Light Source	Removal and TOC Decay	References
Cephalexin (50 mg/L)	Chalcopryrite (1 g/L)	IrO ₂ /air diffusion cathode	0.05 M Na ₂ SO ₄ , pH: 3, AFR: 0.6 L/min, I = 125 mA	6 W UVA fluorescent	100% removal (15 min) 92% TOC decay (300 min)	[16]
Bezafibrate (10 mg/L)	Fe-MOFs (0.05 g/L)	IrO ₂ /air diffusion cathode	0.05 M Na ₂ SO ₄ , pH: 5.1, AFR: 1 L/min, I = 100 mA	150 W Xe lamp (λ > 400 nm)	92% removal (90 min) 61% TOC decay (240 min)	[48]
Thiamphenicol (50 mg/L)	Pyrite (2 g/L)	IrO ₂ /air diffusion cathode	0.02 M Na ₂ SO ₄ , pH: 3.95, AFR: 1 L/min, I = 100 mA	6 W UVA fluorescent	100% removal (60 min) 85% TOC decay (360 min)	[81]

TOC: total organic carbon, AFR: air flow rate, UVA: Ultraviolet A, MOFs: metal–organic frameworks.

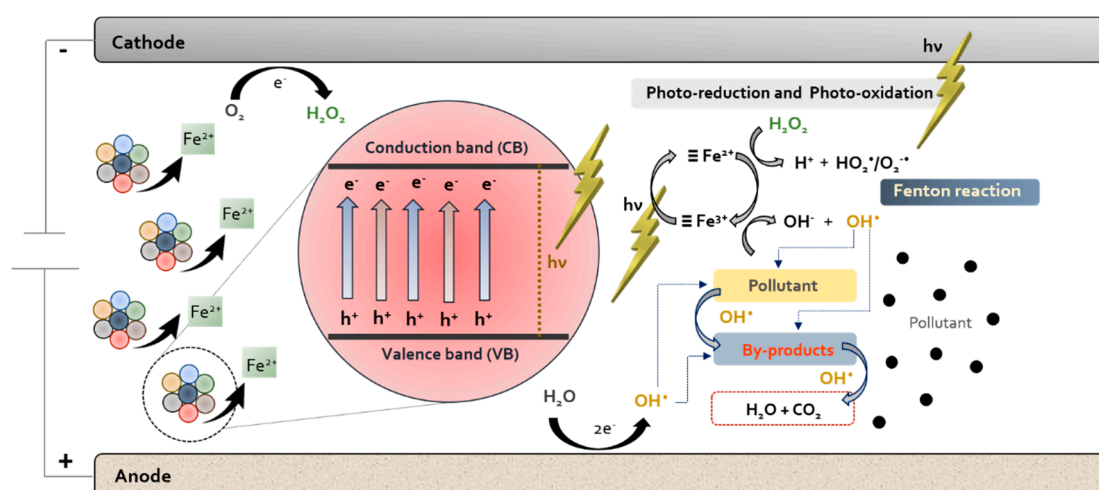
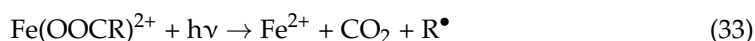


Figure 3. Mechanism of heterogeneous photoelectro-Fenton process.

When absorbed, the energy of the photons can be used to photo-reduce $[\text{Fe}(\text{OH})]^{2+}$ under acidic conditions (Equation (32)) and/or drive photodecarboxylation producing ferrous iron (Equation (33)) [48]:



The majority of research into PEF has been carried out under acidic conditions, with only a small number of studies investigating the potential application at circumneutral pH. Ye et al. [48] described the performance of an Fe-based 2D metal–organic framework (MOF) catalyst for the removal of bezafibrate in sulphate-based medium at pH 5.5 using a single-compartment glass cell upon Xe lamp irradiation, reporting 92% removal—an increase in removal vs. the control experiments. UV photons have been shown to play a key role enhancing charge transfer and promoting Fe (III)/Fe (II) cycling. Studies in urban wastewater spiked with a range of emerging pollutants, bezafibrate, bisphenol A, fluoxetine and naproxen, and at neutral pH showed good removal efficiencies with 93, 85 and 78% removal reported for naproxen, fluoxetine and bisphenol A, respectively, after 90 min treatment. The authors concluded that the presence of organic matter, the high turbidity and the higher initial pH all play a role to reduce bezafibrate treatment.

Thiam et al. [81] analysed thiamphenicol degradation using photoelectro-Fenton process driven with UVA light and pyrite particles as the catalyst source. The regulatory role pyrite plays regarding solution acidification (according to the Equations (26)–(28)) was described to be significant, resulting in enhanced hydroxyl radicals generated via the photo-Fenton reaction. Under optimal conditions, more than 85% TOC decay was achieved after 360 min treatment, noted to be around a three-fold increase in comparison to the electro-Fenton process.

8. Conclusions and Future Perspectives

This review describes the present trends in the use of heterogenous catalysts for the removal of pharmaceuticals from aquatic environments, discussing the critical role of the parameters driving the electro-Fenton process. Although progress has been made with nano-engineered catalysts, high operating costs related to energy consumption, relatively slow degradation processes, and issues with reactor scale-up and catalyst re-use remain major challenges for this emerging field of research. Future studies should be focused on minimising energy consumption, through more efficient electrochemistry, or coupling with renewable energy generation sources such as photovoltaic panels, which can be easily scaled for industrial applications. The identification of efficient process parameters to

deliver treated waters with high parent compound degradation does not always ensure effluent safety, however, mineralisation is not always required—careful attention should be paid to reducing the toxicity levels of treated water, and/or enhancing bio-availability via pre-treatment before wastewater treatment through biological process.

To date, academic research has focused on the initial developments of novel innovative wastewater treatment technologies for the removal of pharmaceuticals from simulated water under batch conditions. However, there is a need to assess efficacy in real water matrices where the presence of natural organic matter (humic and fulvic acids) will undoubtedly scavenge radical species reducing the effective degradation rate. The implementation of heterogeneous-based Fenton process as continuous flow systems is required to ensure potential for scale-up to real water treatment applications.

Significant efforts have been devoted to producing novel solid iron catalysts or iron-functionalised cathodic materials, but more work is needed to evaluate these materials at circumneutral pH in order to ensure higher stability whilst maintaining ability to catalyse Fenton's reaction forming hydroxyl radicals. One area of significant promise is the integration of the electro-Fenton process with conventional technologies, and/or Fenton-based processes and indeed other AOP's, with significant improvements in mineralisation percentages observed. This topic remains a vibrant area for research and through the identification of niche applications could quickly transition to pilots and commercial exploitation.

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